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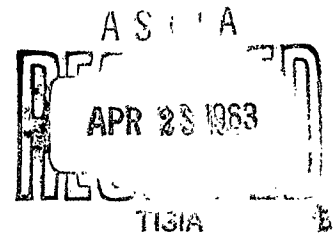
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NUCLEATION OF SILVER ON SODIUM CHLORIDE

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D. Walton, T. N. Rhodin and R. W. Rollins

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### Abstract

The nucleation rate of silver deposited from the vapor phase onto a sodium chloride substrate has been studied as a function of substrate temperature and incidence rate. The experiments have been performed in an ultra-high vacuum system on a substrate cleaved in situ. The results are found to be in agreement with a theory based on the assumption that the critical nucleus is a single atom for high supersaturations and contains three atoms at the lower supersaturations employed. Using the theory a value of 0.4 ev has been obtained for the adsorption energy of silver on sodium chloride. It is also estimated that the activation energy for surface diffusion is less than 0.2 ev, and that the dissociation energy of the cluster of three atoms is 2.1 ev.

## Introduction

In the formation of vapor deposits there is reason to believe that in most cases the critical nucleus is very small, containing less than five to seven atoms. For such small nuclei the classical nucleation rate expressions are not valid. An alternate expression which is also valid for small clusters of atoms has been derived in a previous publication<sup>1</sup> in which the nucleation rate is given in general by,

$$I_{n^*} = N_0 a_0^2 \left( \frac{R}{v N_0} \right)^{n^*} \left[ \exp \left( (n^*+1) Q_{ad} + E_{n^*} - Q_D \right) / kT \right] \quad (1)$$

where,

$n^*$  = number of atoms in the critical nucleus

$R$  = rate of incidence from the vapor,  $\text{cm}^{-2} \text{sec}^{-1}$

$N_0$  = number of adsorption sites per  $\text{cm}^2$  of surface

$v$  = a frequency of vibration

$Q_{ad}$  = binding energy of a single atom to the surface

$E_{n^*}$  = dissociation energy of the critical nucleus

$Q_D$  = activation energy for diffusion

$a_0$  = distance covered in a single diffusion jump.

At the high supersaturation limit the critical nucleus becomes a single atom. If this is so, then  $E_{n^*} = 0$ , and the nucleation rate becomes

$$I_1 = N_0 a_0^2 \left( \frac{R}{v N_0} \right) \exp (2Q_{ad} - Q_D) / kT \quad (2)$$

As the supersaturation is lowered, a point will be reached at which the nucleation rate is no longer given by Eq. (2). Equation (2) is the rate of formation of pairs and will only hold as long as a pair is stable, and as long as its probability of decaying is less than its probability of growing, i.e., when its probability of decay is less than one-half. The nucleation rate to a first approximation is calculated in general as the rate of formation of the smallest cluster whose probability of decay is less than one-half. If the supersaturation is lowered so that a pair becomes unstable because the binding of one atom to another is insufficient to prevent the decay of the pair into two single atoms before it is joined by a third, then a configuration with two bonds per atom can become the smallest stable cluster, i.e., the smallest cluster whose probability of decay is less than one-half. Of the large number of possible configurations which have a minimum of two bonds per atom those with the smallest number of atoms will be favored because the concentration of a cluster decreases rapidly with its size. The smallest cluster with the required minimum of two bonds is a triangular configuration of three atoms (Fig. 1b). It can be seen (Fig. 1b) that this will lead to an orientation of the film such that a (111) plane is parallel to the substrate. However, when face centered cubic metals are deposited on a sodium chloride cleavage face the resultant orientation is a

(100) plane parallel to the surface. This orientation will result if the cluster consists of four atoms in a square (Fig. 1d). Thus it can be concluded that in this case the nucleation rate is given by the rate at which the four atom cluster is formed. The critical nucleus in this case will be the configuration of three atoms shown in Fig. 1c, and the nucleation rate is given by

$$I_3 = 4R \left( \frac{R}{N_0} \right)^3 \left[ \exp^{-(4Q_{ad} + E_3 - Q_D)/kT} \right] \quad (3)$$

where  $E_3$  is the dissociation energy of the cluster shown in Fig. 1c.

( $N_0 = 4/a_0^2$  for NaCl, if it is assumed that the binding forces between the adsorbed atom and the substrate are not directional.)

The temperature at which the transition occurs from one nucleus to the other can be obtained by equating Eqs. (2) and (3). Thus the transition temperature is

$$T = \frac{(1/2 E_3 + Q_{ad})}{k \ln (R/\sqrt{N_0})} \quad (4)$$

It is not clear why the triangular configuration is less favored.<sup>2</sup> In fact it does occur in sufficient concentration for a (111) orientation to be detected when gold is deposited on NaCl.<sup>3</sup> Nevertheless, it is probably adequate to neglect the appearance of the (111) orientation and use Eq. (3) for the nucleation rate.

If the supersaturation is lowered still further a point will be reached at which the smallest stable cluster with a minimum of two bonds has a probability greater than one-half of decaying. Equation (3) is then no longer valid, and larger critical nuclei must be considered. However, this will not be done here.

The purpose of this work is to examine the applicability of Eqs. (2) and (3) to the formation of a silver deposit on NaCl. Specifically the following points will be considered:

a) In the region where Eq. (2) holds the nucleation rate is proportional to  $R^2$  and where Eq. (3) is valid it is proportional to  $R^4$ .

b) The pre-exponential terms may be calculated and compared with the measured values.

c) The values of the individual terms in the exponential may be determined since there are three equations available, 2, 3, and 4, and three unknowns. In addition, a useful independent check on these values can then be obtained in the following way:

It is characteristic of the formation of the deposit that as each island grows it acts as a sink for single atoms in its immediate neighborhood. Thus each growing particle depletes a surrounding region. The radius of this region is to a first approximation the average distance an atom may diffuse on the surface before it evaporates the diffusion distance. The diffusion distance is given by<sup>4</sup>



$$d = a_0 \exp(Q_{ad} - Q_D) / 2kT . \quad (5)$$

As nucleation proceeds and more particles appear less surface is available for nucleation. Nucleation should in fact stop when the depleted regions overlap. If this is true then the diffusion distance, and hence  $(Q_{ad} - Q_D)$  may be determined from the saturation number of particles.

d) Finally the epitaxial temperature should be related to the substrate temperature and the incidence rate by an expression<sup>2</sup> similar to Eq. (4). It is identical except that instead of  $1/2 E_3$  the energy of a single bond  $U$  between a single atom and the growing cluster should appear

$$T_e = \frac{U + Q_{ad}}{k \ln (R/rN_0)} \quad (6)$$

The energy of the single bond,  $U$ , should be less than or equal to  $1/2 E_3$ , but greater than the energy of a single bond in the bulk crystal, since for a metal the binding energy of an atom to the cluster can be expected to vary inversely with the size of the cluster.

This expression is derived by assuming<sup>2</sup> that if an atom is bound to the growing particle by a single bond and does not leave the particle before another atom arrives, a single orientation will not be possible. On the other hand, if it must be bound by two bonds to be

stable then an orientation will be produced. Thus the simple argument presented above ignores the possibility that the atom may diffuse to a more favorable position on the cluster.

### Experimental

Basically the experiments consist of determining the nucleation rate as a function of substrate temperature and incidence rate. To reduce the problems induced by uncontrolled contamination the experiments are carried out in an ultra-high vacuum system on a substrate cleaved in situ.

The system is shown schematically in Fig. 2. The vacuum system is a 3" bakeable metal system and is capable of a base pressure of between  $2$  and  $3 \times 10^{-10}$  mm of Hg after baking out at  $300^\circ\text{C}$  for approximately six hours.

The source consisted of a tantalum strip with a depression in the center which contains the silver. The source was heated by passing a current of about 15 amperes through the tantalum strip. The temperature was measured by a chromel-alumel thermocouple spot-welded to the depression in the tantalum strip. It was found to indicate a temperature at the melting point of silver within  $3^\circ\text{C}$  of the true melting point. After suitable outgassing it was possible to evaporate a silver at a suitable rate with a pressure in the system less than  $1 \times 10^{-9}$  mm of Hg. Detailed views  $90^\circ$  apart are in Fig. 3.

The NaCl substrate was a single crystal about 5 mm x 5 mm x 3 cm held in a copper block by a spring. The copper block was heated externally by a nichrome heater and its temperature measured by a chromel-alumel thermocouple.

The substrate was cleaved by a razor blade introduced into the system through a stainless steel bellows.

The experimental procedure used was to bring the source to temperature before the crystal was cleaved. The condensation of silver effectively started when the crystal cleaved. It was continued for a specified length of time, and stopped by turning off the current to the source.

The crystal with the deposit was then removed from the system, the deposit was shadowed with platinum, backed with carbon and the substrate dissolved away. The replica produced in this way was examined in the electron microscope where the number of islands of deposit were counted. This number divided by the time of the evaporation yielded the nucleation rate.

For this procedure to yield the true nucleation rate it was important that the saturation effects referred to in the introduction be avoided. This was verified by shielding half the crystal with the razor blade midway through the evaporation and determining whether the concentration of deposit on one half was twice that on the other, or not.

### Results and Discussion

Before discussing the results in detail it is well to review the major apparent sources of experimental error.

It is obvious that particles of dimensions smaller than the resolution limit of the microscope were not counted. In practice even those slightly larger than this could not be detected because of the grain size of the particles of shadowing material. A second source of error appeared to be associated with the stripping process: There was some reason to believe that particles smaller than about 40A in size disappeared. From the length of the shadow it was determined that the particles were about as high as they were wide. Thus they were growing uniformly in all directions, and at steady state their linear dimension must be proportional to the cube root of the time. In the results to be quoted the largest particles observed were between 100A and 200A in width so that the particles which went undetected must have been growing for a fraction of the time of the experiment which was

$$\left(\frac{40}{100}\right)^3 = .064$$

Therefore the error due to not counting particles smaller than 40A is not more than about 6%.

A third possible source of error is due to the

effect of residual gas in the vacuum system. However during preliminary experiments the system pressure during an evaporation lasting five minutes varied from run to run by a factor of 10 (from  $8 \times 10^{-10}$  mm to  $3 \times 10^{-9}$  mm) without any noticeable effect on the deposit.

The substrate and source temperature were held to  $\pm 0.5^\circ\text{C}$ , and the error due to fluctuations in these temperatures is negligible.

Finally the effect of impurities and imperfections in the crystal in nucleating the deposit should be considered. The effect of steps is preferentially nucleating the deposit is shown in Fig. 6. It is clear that this effect can be readily identified and eliminated as a source of error by the simple expedient of counting between the steps. Point imperfections on the surface such as emergent dislocations or impurity atoms cannot be identified as readily. However, it is possible to discount the effect of these defects in the present work since some care was taken to work at particle densities which were as high as possible without saturation effects becoming a problem.

Let the number of defect sites per unit area of surface be  $N_d$ , and assume that  $N_d \ll N_0$ . Let the additional binding energy of a cluster of size  $n$  to the site be  $Q_n$ . Then at equilibrium the number of clusters of size  $n$  on defect sites per unit area of surface,  $N'_n$ , will be, assuming  $N'_n \ll N_d$

$$\frac{N'_n}{N_d} = \frac{N_n^0}{N_o} e^{Q_n/kT} \quad (7)$$

The nucleation rate is

$$I' = N'_{n*} \Gamma_{n*}^+ \quad (8)$$

where  $\Gamma_{n*}^+$  is the rate of arrival of single atoms at the nucleus of size  $n^*$ .

Thus  $I'$  can be written

$$I' = \frac{N_n^0}{N_o} e^{Q_n/kT} \quad (9)$$

since  $I = N_{n*} \Gamma_{n*}^+$

The rate  $I'$  is the rate per unit area of surface. However, what is probably more significant is that the time to consume a fixed fraction of the available defect sites is a factor  $e^{Q_n/kT}$  times the time to exhaust the same fraction of the normal sites. This is significant for the following reason. The total nucleation rate on the free surface is  $I + I'$ . For  $I'$  to be a significant correction,

$$N_d/N_o \approx e^{Q_n/kT} \quad (10)$$

If  $N_d$  is less than  $10^9 \text{ cm}^{-2}$  then the imperfections can be neglected since a typical particle density is  $10^{10} \text{ cm}^{-2}$ . If  $N_d$  is greater than about  $10^{12} \text{ cm}^{-2}$  they

would be detectable by other means. Thus the defects are only troublesome if they occur in concentrations of  $10^{10}$ - $10^{11}$   $\text{cm}^{-2}$ . But if this were so,  $Q_n$  from Eq. (10) would have to be of the order of 0.3-0.4 ev. The pre-exponential would be lower by a factor of  $10^{-4}$ - $10^{-5}$  and the experimental results would no longer agree with Eqs. (2) and (3). \*

The results are shown in Fig. 5 and Table I. The source used for the incidence rates of  $6 \times 10^{13}$   $\text{cm}^{-2}$   $\text{sec}^{-1}$  and  $2 \times 10^{13}$   $\text{cm}^{-2}$   $\text{sec}^{-1}$  was accidentally destroyed before the absolute value of the incidence rate could be determined. The values quoted were calculated from the geometry of the system using vapor pressure data from Honig.<sup>6</sup> However, the relative magnitudes are exact, and correspond to a ratio of three in the relative incidence rates.

Using a second source, nucleation rates were determined at the lower substrate temperatures. The incidence rate was measured in this case by weighing the silver deposited for a fixed length of time and was found to be  $1 \times 10^{13}$   $\text{cm}^{-2}$   $\text{sec}^{-1}$ .

The results in Fig. 2 yield an "activation energy" above the transition temperature of 3.7 ev, a transition temperature between 250 and 240°C, and below this an "activation energy" of 0.9 ev.

A change in incidence rate of a factor of three above the transition temperature resulted in a change of the nucleation rate of 100. Below the transition

temperature a change in nucleation rate of a factor of six corresponded to a change in the incidence rate of about two. In this latter temperature range two different sources are being compared so the ratio of the incidence rates given is only approximate.

As a further check it is possible to substitute values for  $R$ ,  $v$ , and  $N_0$ , in the appropriate equations and compare the nucleation rate obtained in this way with the experimental value. On a perfect sodium chloride cleavage face there are  $6.6 \times 10^{14}$  sodium atoms. If it is assumed that the silver atom is bound to the surface by non-directional forces there are four adsorption sites around each sodium atom,<sup>2</sup> and  $N_0$  is then  $2.6 \times 10^{15}$  atoms/cm<sup>2</sup>. A value for  $v$  of  $10^{12}$  sec<sup>-1</sup> is probably appropriate on surfaces. In fact using a value of  $Q_{ad}$  of 0.4 ev, obtained from the experimental results, and making the assumption that the adsorbed atom is a harmonic oscillator whose potential energy is equal to this value at a distance from the potential energy minimum equal to the radius of a silver atom, the same frequency is obtained. This to some extent justifies the above choice. With these values the calculated value of the pre-exponential is  $3 \times 10^{-27}$  cm<sup>-2</sup> sec<sup>-1</sup>, and the measured value is  $3 \times 10^{-28}$  cm<sup>-2</sup> sec<sup>-1</sup> for an incidence rate of  $6 \times 10^{13}$  cm<sup>-2</sup> sec<sup>-1</sup>.

For an incidence rate of  $1 \times 10^{13}$  cm<sup>-2</sup> sec<sup>-1</sup>, below the transition temperature the value of  $4R(R/vN_0)$  is



$1.5 \times 10^{-1} \text{ cm}^{-2} \text{ sec}^{-1}$ , compared to the measured value for the pre-exponential of  $6 \times 10^{-1} \text{ cm}^{-2} \text{ sec}^{-1}$ .

Considering the assumptions made in deriving Eqs. (2) and (3), and the errors involved in the experiment, the agreement between the two is adequate.

Above the transition temperature the plot of  $\ln I$  against  $1/T$  yields

$$(4Q_{\text{ad}} + E_3 - Q_D) = 3.8 \pm 0.2 \text{ ev} .$$

From the transition temperature

$$(Q_{\text{ad}} + 1/2E_3) = -kT \ln (R/vN_O) = 1.5 \pm 0.1 \text{ ev}$$

and from the results below the transition temperature

$$(2Q_{\text{ad}} - Q_D) = 0.7 \pm 0.1 \text{ ev} .$$

These results are consistent with values of  $Q_{\text{ad}} = 0.4 \text{ ev}$  and  $E_3 = 2.1 \text{ ev}$ . Unfortunately the accuracy is insufficient to do more than place a limit on  $Q_D$ .  $Q_D$  appears to be less than  $0.2 \text{ ev}$ .

An independent check can be obtained from the diffusion distance, as previously discussed. The maximum density of particles of deposit at  $220^\circ\text{C}$  is  $10^{11} \text{ cm}^{-2}$ . Thus  $(Q_{\text{ad}} - Q_D) = 0.33 \pm 0.02 \text{ ev}$ , which is consistent within experimental error with the above values.

Thus the agreement between theory and experiment can be considered adequate considering the experimental errors involved and the assumptions made in deriving Eqs. (2) and (3).

The effect of substrate temperature on the orientation of the deposit is shown in Fig. 6. The deposits formed at 48°C and 150°C show considerably less orientation than the deposit formed at 220°C. However, the lower temperature deposits are by no means amorphous, thus diffusion effects are important, and a rigorous treatment of the epitaxial temperature should take these into account. Neglecting this effect it is possible to place limits on the energy of the single bond to the growing cluster, using Eq. (6) and this energy appears to lie between 0.7 ev and 0.9 ev. This is considerably higher than the single bond energy in the crystal, thus it may be concluded that it represents the binding energy of a single atom to a very small cluster.

### Conclusions

1. It is possible to develop an expression for the nucleation frequency of condensation of a metal vapor in terms of the structure of the critical nucleus and its configuration on the surface. The validity of this expression has been determined experimentally for the deposition of silver on the cleavage face of sodium chloride for conditions where the critical nucleus is expected to be very small.

2. Surface imperfections strongly influence the nucleation rate but their effect can be resolved in terms of exposure time and substrate temperature. The observed effects of surface temperature on the stability and orientation of the silver deposit can also be interpreted in terms of the model.

### Acknowledgments

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TABLE I

Substrate Temp. °K	R $\text{cm}^{-2}\text{sec}^{-1}$	Time secs	# of Particles/ $\text{cm}^2$	I $\text{cm}^{-2}\text{sec}^{-1}$
552	$6 \times 10^{13}$	300	$5.2 \times 10^9$	$1.7 \times 10^7$
533	"	"	$8.7 \times 10^{10}$	$2.9 \times 10^8$
541	"	600	$3.4 \times 10^{10}$	$5.7 \times 10^7$
548	"	"	$2.7 \times 10^{10}$	$4.5 \times 10^7$
539	"	"	$6.4 \times 10^{10}$	$1.1 \times 10^7$
523	$2 \times 10^{13}$	600	$9 \times 10^9$	$1.5 \times 10^7$
514	"	"	$3.3 \times 10^{10}$	$5.5 \times 10^7$
513	"	1200	$6 \times 10^{10}$	$5 \times 10^7$
503	"	600	$4 \times 10^{10}$	$6.6 \times 10^7$
502	$1 \times 10^{13}$	1200	$1.2 \times 10^{10}$	$1.0 \times 10^7$
514	"	2400	$1.9 \times 10^{10}$	$7.9 \times 10^6$
493	"	1800	$2.7 \times 10^{10}$	$1.5 \times 10^7$
492	"	1200	$1.8 \times 10^{10}$	$1.5 \times 10^7$

### List of Figure Captions

Fig. 1 - Two dimensional clusters.

Fig. 2 and 3 - Experimental apparatus.

Fig. 4 - Nucleation on imperfections.

Fig. 5 - Nucleation rate vs. substrate temperature.

Fig. 6 - Electron diffraction patterns of silver deposited  
on a cleaved sodium chloride substrate at 48°,  
at 150°C and at 220°C. (Incidence rate,  $10^{14}$  cm<sup>-2</sup>  
sec<sup>-1</sup>)

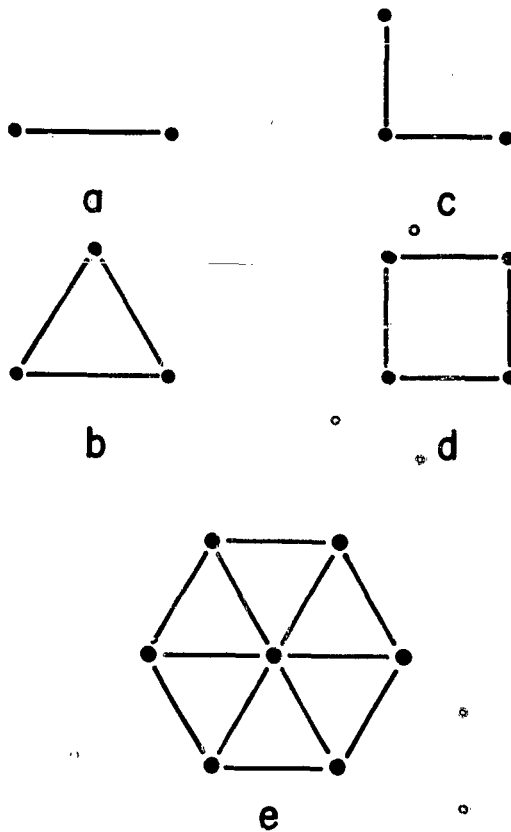
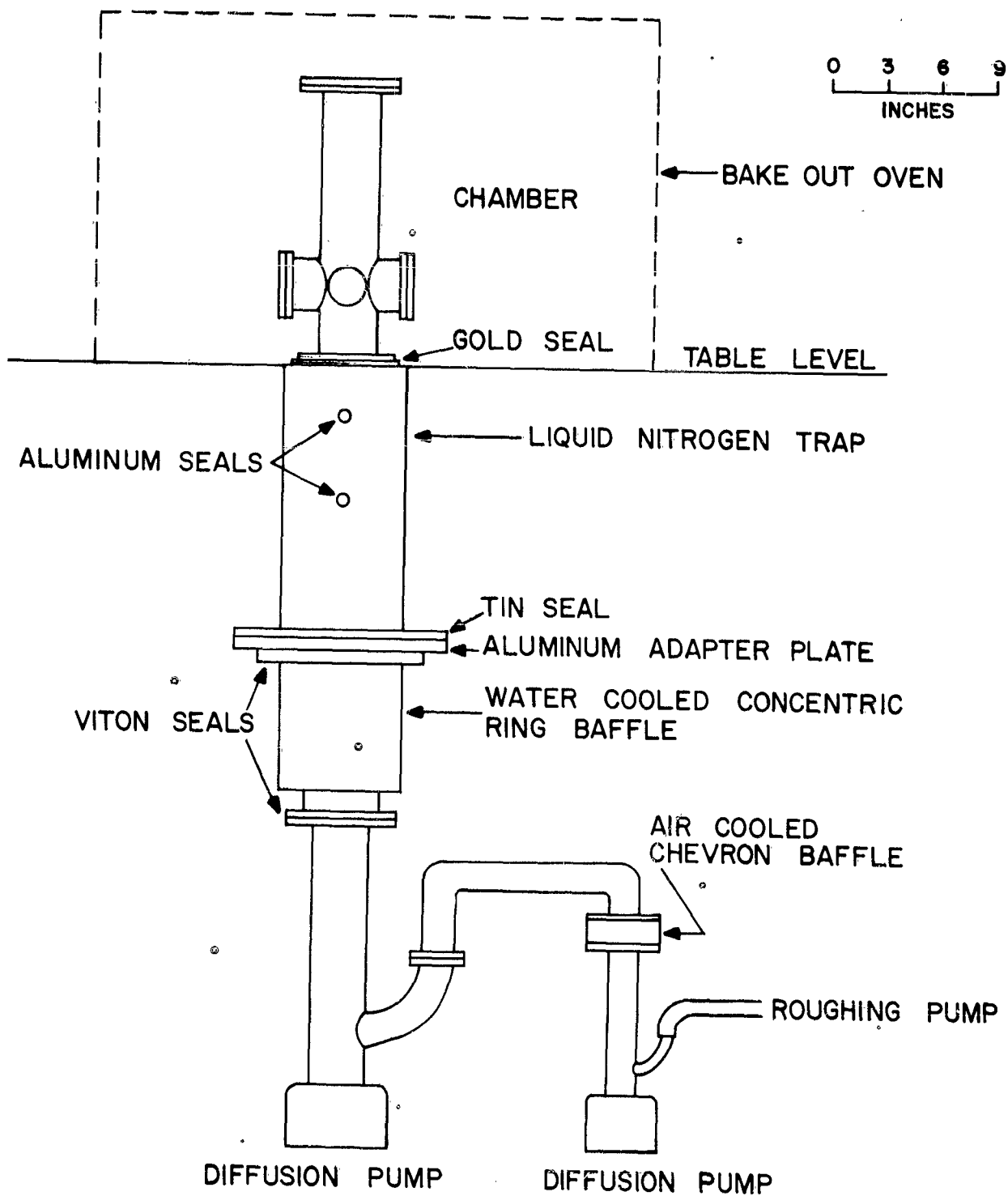
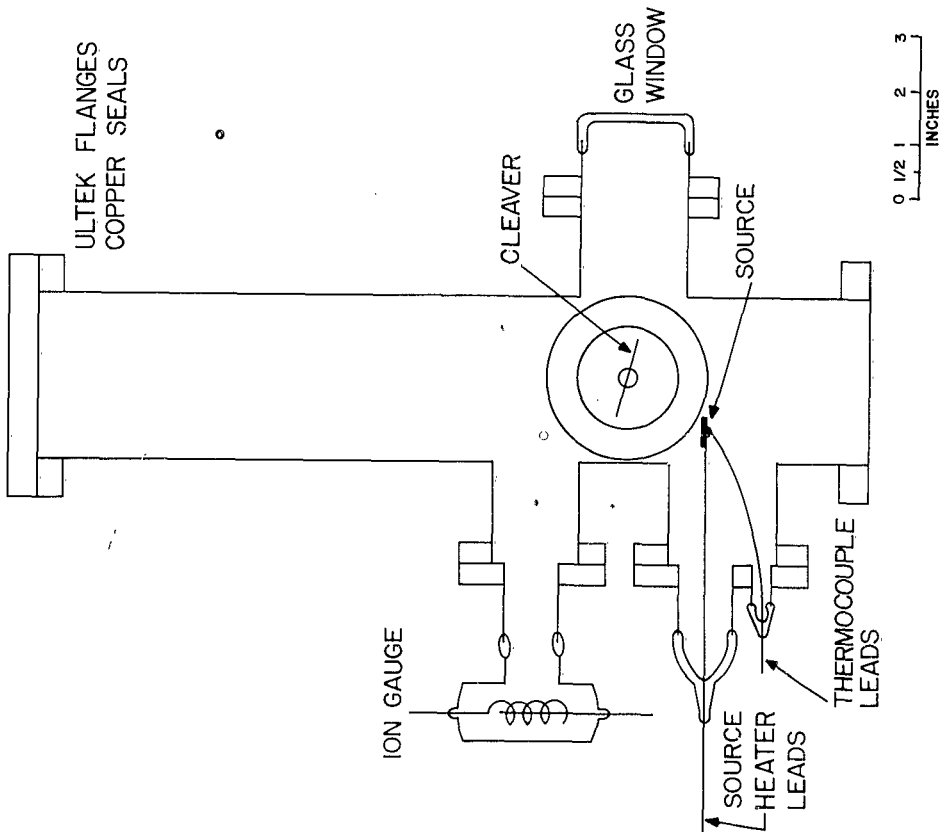
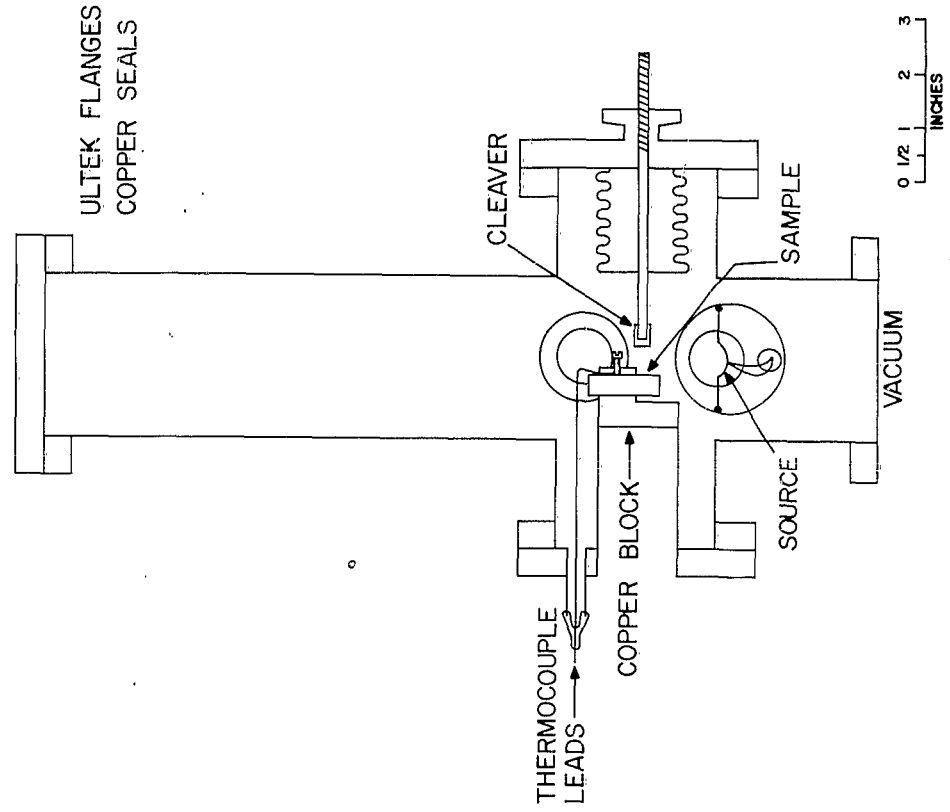
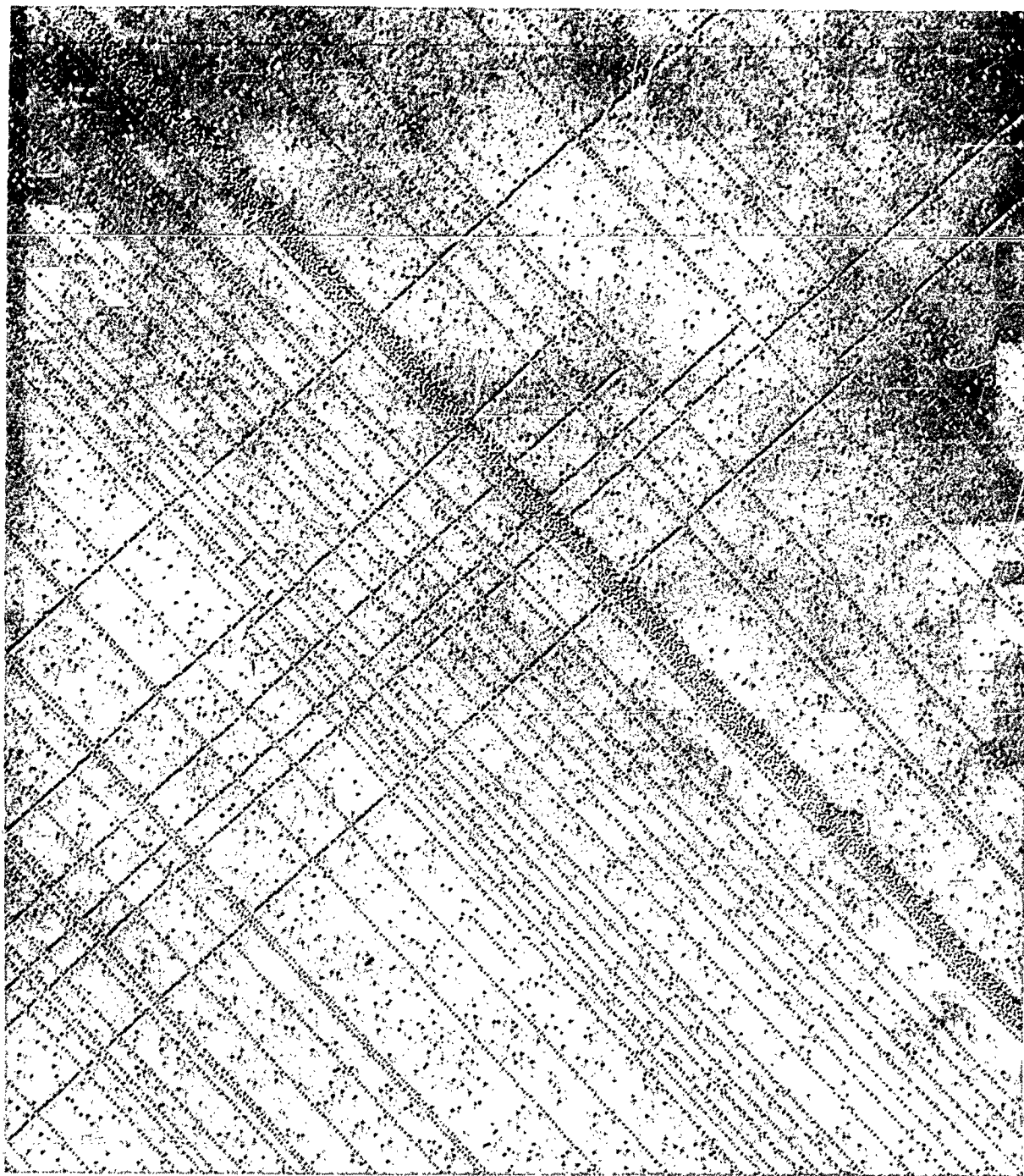


FIG. 1









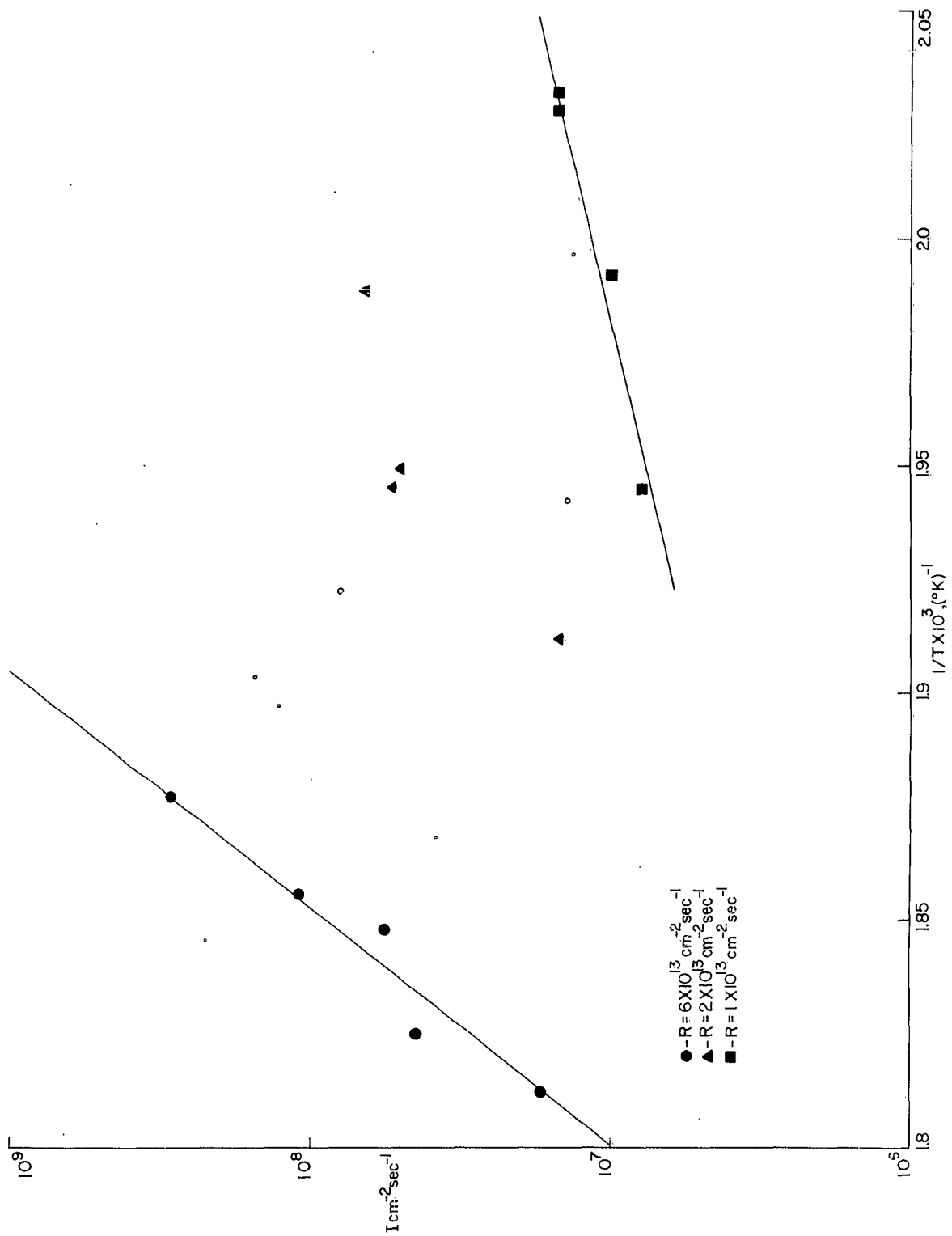


FIGURE 4

